



Carbon nanodots/WO₃ nanorods Z-scheme composites: Remarkably enhanced photocatalytic performance under broad spectrum



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ABSTRACT

The search for low-cost, earth-abundant and environmentally friendly photocatalysts that can efficiently function over the entire UV–vis–NIR spectrum remains one of the most pressing challenges in the photocatalytic elimination of pollutants from water. Herein, we accurately designed and fabricated a direct Z-scheme carbon nanodots/WO₃ nanorods composite (CDots/WO₃) with highly enhanced photo-response and broad-spectrum photocatalytic activity. Under ultraviolet, visible, near-infrared (UV, Vis, NIR) irradiation, respectively, the removal efficiencies of rhodamine B (RhB) always decreased in the order CDots/WO₃ (97.1, 99.1, 61.2%) > prepared WO₃ nanorods (66.6, 69.1, 22.4%) > commercial WO₃ nanoparticles (22.1, 11.6, ~0%). Additionally, reaction rate constants of 0.4030 and 0.2889 h^{−1} were achieved by the CDots/WO₃ nanocomposites when photo-oxidizing tetracycline hydrochloride (TCH) and phenol, respectively, both of which were ~2.9 times higher than those for WO₃ nanorods. This excellent photocatalytic performance was ascribed to synergistic effects, including the highly dispersed carbon nanodots on the surface of the WO₃ nanorods and efficient charge separation induced by the heterostructure formed between carbon nanodots and WO₃ nanorods. Accordingly, a mechanism was proposed to account for the photocatalytic reaction process. The prepared catalyst showed no obvious change in its photocatalytic performance or other chemical properties after 5 cycles of use. Therefore, the carbon nanodots/WO₃ nanocomposites may represent a new strategy for the full-spectrum utilization of solar light, providing an invaluable methodology for the remediation of current water-pollution issues.

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1. Introduction

Efficient semiconductor photocatalysis is a promising and effective strategy for purifying water contaminated by various environmental pollutants [1]. To date, a wide variety of semiconductor materials have been developed, including ZnO, TiO₂, C₃N₄, Bi₂WO₆, CdS and Ag₂O, among others [2–6]. However, two key factors seriously restrict the further application of these photocatalysts, namely, the low solar-light utilization efficiency and rapid electron–hole recombination [7]. Therefore, numerous efforts have been made to solve these problems.

Regarding solar-energy utilization, the preparation of semiconductor photocatalysts that can harvest the entire spectrum of solar light, from ultraviolet (UV) to near-infrared (NIR) wavelengths, while achieving efficient solar-energy conversion, remains one of the most important challenges [6,8]. Recently, several UV–vis–NIR-

active catalysts have been reported, including CdS, Ag₂O, BiOI and carbon nanodots (CDots) [4,6,9–11]. Among them, CDots, a new member of the carbon family consisting of particles with sizes below 10 nm, have attracted increasing interest because of unique properties including their large two-photon absorption cross sections, up-conversion ability, low toxicity, high biocompatibility and excellent electron-transfer and electron-reservoir properties [12,13]. Accordingly, CDots can be employed as a co-catalyst to build surface separation centers for electrons and reduce the recombination rate of charge carriers. It has been reported that CDots/TiO₂ nanotube arrays [14], CDots/Ag₃PO₄ [15], CDots/H-γ-TaON [8], CDots/BiOX (X = Cl, Br and I) [16], CDots/Bi₂WO₆ [5] and CDots/g-C₃N₄ [12] composites as well as CDots/CdS [17] heterostructures exhibit enhanced photocatalytic activity and structural stability, compared with single-species catalysts, for the photo-decomposition of organic compounds, evolution of hydrogen by water splitting or solar-light-driven conversion of CO₂ to methanol. The conjugated π structure of the CDots in these composites plays an important role in their improved photocatalytic activities [8]. Therefore, CDots could potentially function as a co-

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catalyst, capable of harnessing a broader range of visible or NIR light to enhance the performance of the main photocatalysts.

Recently, one-dimensionally (1-D) nanostructured semiconductor photocatalysts have received extensive attention, and are considered to be ideal photocatalytic materials because their reduced grain boundaries can shorten the transmission path of the photo-generated charges and realize the effective separation of electron–hole pairs [18–21]. Their high crystallinity and abundance of surface active sites are conducive to photo-absorption and redox reactions, and allow them to efficiently gather organic pollutants in wastewater [20,22]. Considering the above-mentioned properties and previous reports regarding 1-D nanomaterials, it is likely that they have the potential to achieve higher photocatalytic activity than nanoparticles.

Among the wide range of 1-D nanostructured semiconductors, tungsten oxide (WO_3) nanorods have been regarded as particularly suitable candidates because of their stable physicochemical properties, resilience to photo-corrosion effects, relatively narrow band-gap energy (2.4–2.8 eV) and the high oxidative power of their valence band (VB) holes [20,23]. In addition, in contrast with WO_3 nanoparticles, WO_3 nanorods, with their high specific surface area, provide more active sites and attachment points, which is conducive to the formation of composite photocatalysts. In spite of these advantages, the photocatalytic activity of WO_3 nanorods alone is still limited by several critical drawbacks. First, their intrinsic band-gap energy (2.4–2.8 eV) severely limits their solar-light utilization efficiency [23]. Second, they usually suffer from a high recombination rate of the charge carriers at the surface, which are slow to participate in interface redox reactions [20]. Last, their relatively low conduction band (CB) level does not provide a sufficient potential to react with strong electron acceptors, which directly results in fast recombination and thus lower photocatalytic activity. Therefore, considerable efforts have been devoted to the development of a novel WO_3 nanorods-based photocatalyst that can efficiently utilize a wide spectrum of solar-light irradiation.

It has already been confirmed that CDots can efficiently enhance the photocatalytic and photo-electrochemical performance of WO_3 under visible-light irradiation [24,25]. Shi et al. [24] showed that a CDots/ WO_3 electrode had a higher photo-current and photo-electric conversion efficiency than the corresponding WO_3 electrode. Yang et al. used IO_3^-/I^- as a shuttle redox mediator to transfer the photo-generated electrons in the CB of WO_3 to the VB of CDots, and found that this Z-scheme was an effective strategy to improve the photocatalytic performance of WO_3 [25]. Thus, on the basis of these reports, it is plausible that the CDots/ WO_3 nanorods Z-scheme heterostructure could be used as an efficient photocatalyst. However, little is known about the photocatalytic activity and mechanism of CDots/ WO_3 nanocomposites over the UV–vis–NIR broad spectrum. Is a direct Z-scheme system still present in CDots/ WO_3 in the absence of redox mediators such as IO_3^-/I^- ? It is desirable to construct direct Z-scheme systems from CDots/ WO_3 nanorods composites to enhance the photo-response and broad-spectrum photocatalytic performance of WO_3 , and to reveal the corresponding photocatalytic oxidation mechanisms accurately and in detail.

To the best of our knowledge, there is no previous report of simultaneous broad-spectrum light utilization and efficient charge separation by a system comprising CDots coupled with WO_3 nanorods to form an all-solid-state direct Z-scheme heterojunction. Herein, for the first time, we synthesized UV-, visible- and NIR-light-driven CDots/ WO_3 nanorods composite photocatalysts, ensuring the fast interior transport, surface separation and effective solar-light absorption of the carriers so as to enhance the photocatalytic activity. The WO_3 nanorods were used as a supporting material, leading to the homogeneous dispersion of the

prepared CDots nanoparticles on the nanorod surfaces to form CDots/ WO_3 nanorods Z-scheme heterostructures with spectrum-versatile activity, i.e., UV, visible and NIR. The photocatalytic performance of the catalysts was evaluated by decomposing Rhodamine B (RhB), tetracycline hydrochloride (TCH) and phenol in aqueous solutions under UV, visible and NIR irradiation, respectively. The composites exhibited superior photocatalytic activity, which was mainly ascribed to the synergistic effect between WO_3 nanorods and CDots. Subsequently, a possible photocatalytic mechanism for the broad-solar-spectrum activity of the CDots/ WO_3 nanorods heterostructures was proposed. Hence, this work may be of interest to both materials scientists and those working in the area of catalyst design.

2. Experimental

2.1. Catalysts preparation

All chemicals were analytical grade without further purification. A common electrochemical method was used to synthesize CDots. WO_3 nanorods was prepared via a simple hydrothermal method that according to previous reports with some modified [26]. The detailed processes can be found in Supplementary materials.

CDots/ WO_3 nanorods composites prepared via an oil bath reflux. First, 0.1 g WO_3 nanorods dissolved into 80 mL CDots aqueous solution to form a homogeneous mixture. Then, the mixture was transferred to oil bath pot and run at 90 °C for 3 h and the heterostructure was obtained. Last, the resulted samples were washed with ultrapure water for 3 times and dried at 60 °C. For comparison, a series of CDots/ WO_3 nanocomposites were prepared by adding different content of CDots (wt%), which were accordingly denoted as X wt% CDots/ WO_3 (X = 0.2, 0.4, 0.8 and 1.2). In this paper, we used CDots/ WO_3 instead of 0.8 wt% CDots/ WO_3 , as it was proved to possess the highest photocatalytic activity and was most intensively studied.

2.2. Characterization

The morphology and crystal structure of prepared samples were investigated via the Scanning Electron Microscopy (SEM, JEOL JSM-7001F), Transmission Electron Microscopy (TEM), and High-Resolution TEM (HRTEM) (via a 200 kV FEI-Tecna F20, USA) measurements. Accordingly, the corresponding 2D fast Fourier transform (FFT) pattern was obtained via Digital Micrograph. The XRD patterns were acquired with a powder X-ray diffraction (XRD, Bruker D8, Germany) equipped with $\text{Cu K}\alpha$ radiation. X-ray photo-electron spectroscopy (XPS) was conducted via an X-ray photo-electron spectroscopy using an Al $\text{K}\alpha$ ($h\nu = 1486.6$ eV) radiation excitation source. All of the obtained spectra were calibrated against the C 1s signal at $\text{BE} = 284.6$ eV. The UV–vis–NIR diffuse reflection spectra (DRS) was taken on a Lambda 750 spectrophotometer (Perkin Elmer). Raman spectra was obtained by using an HR 800 Raman spectroscope (Horiba Jobin Yvon, France). The Fourier transform infrared (FT-IR) spectrums were investigated by a FT-IR spectrometer (Spectrum One, Perkin Elmer). The photoluminescence (PL) spectra were carried out on a luminescence spectrometer (Cary Eclipse, Varian Medical Systems, USA). The electron spin resonance (ESR) spectra were performed on a Bruker model ESR JES-FA200 spectrometer by using the spin-trap reagent DMPO (5,5-dimethyl-1-pyrroline N-oxide, Sigma Chemical Co.) in water (for hydroxyl radical) and methanol (for superoxide radical).

2.3. Photocatalytic measurements

The light source for photocatalytic reaction was a 150 W Xenon lamp (CEL-HXF 300, Beijing Education Au-light Co., Ltd.). Three

different filter glasses were used to allow the pass-through of UV (320–400 nm, UV light reflection filter: CEL-UVREF), visible (420–780 nm, UV–IR cut-off filter: CEL-UVIRCUT420-780) and NIR light ($\lambda > 780$ nm, IR filter: VISCUT780), respectively (the spectrum and output power of UV, visible and NIR light were shown in Fig. S1 and Table S1). The photocatalytic activity of the as-prepared catalysts under UV, visible and NIR light irradiation were estimated by measuring the degradation rate of RhB (10 mg L^{-1}) in an aqueous solution. Moreover, phenol (20 mg L^{-1}) and TCH (20 mg L^{-1}) were also used as additional target pollutants to eliminate the effect of dye-photo-sensitization. 25 mg photocatalyst were added in a sealed quartz reactor which contained 50 mL aqueous solution with target pollutants. Prior to irradiation, the suspension was magnetically stirred to ensure achieved the adsorption-desorption equilibrium after dark reaction for 60 min. In the process of irradiation, a given volume of suspension was sampled at a certain interval, then was centrifuged immediately to obtain the supernatant for pollutant detection. The reusability and stability of the photocatalysts was measured via repeating the identical experiment for five more times. For comparison, CDots, commercial WO_3 nanoparticles, and prepared WO_3 nanorods were used as photocatalytic references under the same experimental conditions.

In the scavenger quenching experiments, the scavengers used was sodium chromate (VI) (0.05 mM , Sigma, 99.5%) for electron, 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) for $\cdot\text{O}_2^-$ (1 mM , Sigma, 99%), isopropanol (0.5 mM , Sigma) for $\cdot\text{OH}$ and sodium oxalate (0.5 mM , Sigma, 99.5%) for hole. The volume ratio of each scavenger and RhB solution was 1:100 in this experiment. Then, the scavengers were added in to the 50 mL RhB (10 mg L^{-1}) solution before photo-irradiation. After the reaction, the concentrations of RhB were measured. To show a clear comparison, the reaction time for WO_3 and CDots/ WO_3 were 260 and 160 min, respectively, in this experiment.

The concentration of RhB was determined by an UV–vis spectrophotometer according to its absorbance at 554 nm . The TCH concentration was determined by an Agilent 1100 HPLC equipped with a $4.6 \times 250 \text{ mm}$, $5 \mu\text{m}$ Venusil HILIC column, and the wavelength of the UV detector was set at 356 nm . The mobile phase (v/v) consisted of 0.02 M acetic acid (90%) and acetonitrile (10%) at a flow rate of 1.0 mL min^{-1} . The phenol concentration was determined by an Agilent 1100 HPLC equipped with a reverse-phase column (Agilent Eclipse XDB-C18) with 150 mm length and 4.6 mm internal diameter, and the wavelength of the UV detector was set at 270 nm . The mobile phase (v/v) consisted of deionized doubly distilled water (90%) and acetonitrile (10%) at a flow rate of 1.0 mL min^{-1} . Besides, the dissolved organic carbon (DOC) of phenol was carried out by a total organic carbon analyzer (SSM-5000A, Shimadzu Company). Below, both of the DOC and phenol/TCH removals were based on mass removals (mg L^{-1}).

2.4. Electrochemical analysis

The transient photo-current measurements and electrochemical impedance spectroscopy (EIS) were performed on CHI-660e electrochemical workstation (Shanghai Chenhua, China) using a three-electrode configuration and the as-prepared samples as working electrode. The working electrodes were prepared by dip-coating method. 5 mg of the sample was suspended in 5 mL of anhydrous ethanol to produce suspension, which was then spin-coated (2000 rpm) onto a FTO glass electrode. The visible light source is a 150 W Xenon lamp with a cutoff filter ($780 > \lambda > 420 \text{ nm}$). A solution containing 0.1 M Na_2SO_4 aqueous solution was used as the electrolyte.

3. Results and discussion

3.1. Characterization of as-prepared materials

The TEM and HRTEM images showed that the prepared CDots presented an irregular spherical shape (Figs. 1 a and S2A). As seen from the particle-size-distribution histogram (embedded in Fig. 1a), the particle diameters ranged from 2.5 to 5.5 nm with an average diameter of 3.7 nm . The HRTEM image of the CDots (Fig. 1a inset) displayed an obvious lattice fringe with a lattice spacing of 0.321 nm , which corresponded well to the (002) crystal plane of graphitic carbon [5]. Consistently with this, the corresponding 2D fast Fourier transform (FFT) pattern (Fig. S2B) exhibited the hexagonal crystalline structure of the CDots, further indicating their successful synthesis. Meanwhile, another lattice fringe, that of graphene, was also observed (see Fig. S2C) [12], indicating that the prepared CDots had formed from the aggregation of graphite fragments.

The SEM (Fig. 1b) and TEM (Fig. 1c) images of the as-prepared CDots/ WO_3 nanocomposite confirmed that the WO_3 nanorods had a highly ordered, 1-D rod-like structure, with a uniform distribution of the CDots on their surfaces. The HRTEM images (Figs. 1 d and S3C) and FFT patterns (Fig. S3D–F) further confirmed that the CDots and WO_3 nanorods were strongly bound and in close contact, which we attribute to the formation of C–O bonds between them [24]. This intimate contact between the CDots and WO_3 nanorods was presumably beneficial to electron transfer from WO_3 to CDots during photo-excitation, resulting in the reduced probability of electron–hole recombination and the enhanced photocatalytic performance. The HRTEM images also clearly revealed lattice fringes with spacings of 0.370 nm in the nanorods and 0.321 nm in the nanoparticles, which corresponded well to the (020) plane of hexagonal wurtzite-type WO_3 [20,27] and to the (002) spacing of graphitic carbon [5]. Further details of the morphology of the prepared WO_3 nanorods and CDots/ WO_3 are given in Fig. S3.

XRD, Raman, FT-IR and XPS analysis were used to characterize the composition and structure of the prepared materials. As shown in Fig. 2a, the XRD patterns of the CDots reflects three prominent peaks. Among them, the peak at 26° was corresponding to the (002) planes of graphite, and the other two peaks emerged at 22.59° and 18.20° were referring to the amorphous carbon and (103) planes (belongs to hexagonal carbon) [28]. The results indicated the transformation of crystalline graphite into amorphous structure carbon, and the partial conversion of sp^2 -hybridized C=C in the aromatic ring into sp^3 -hybridized C=C in the CDots [28]. Meanwhile, strong XRD diffraction peaks indicated that the WO_3 nanorods and CDots/ WO_3 were highly crystalline (Fig. 2a), with the structure of the hexagonal wurtzite phase (JCPDS file no. 75-2187) [26]. No diffraction peaks for the CDots could be observed in the sample of CDots/ WO_3 because of their low content, relatively low diffraction intensity and fine particle size (shown in Fig. 2a) [29]. In addition, there was no obvious difference between the XRD patterns of WO_3 and CDots/ WO_3 , demonstrating that the presence of CDots negligibly influenced the growth of the nanorods, and that the CDots were only deposited on the surfaces of the WO_3 nanorods rather than entering into the crystal lattice of WO_3 . Furthermore, all the peak intensities slightly decreased as the CDots content was increased from 0.2 to 1.2 wt\% (Figs. 2 a and S4). This decrease possibly occurred because the increased amounts of CDots on the surfaces of the WO_3 nanorods blocked the X-ray irradiation and prevented coherent scattering [29]. When varying the concentration of CDots in the CDots/ WO_3 nanocomposites (Fig. S4), no XRD peak shift was observed, which further indicated that the photocatalysts consisted solely of CDots and WO_3 with no impurities.

In the FT-IR spectrum of the CDots (Fig. 2b), carboxyl, carbonyl and hydroxyl groups can be observed, implying the presence

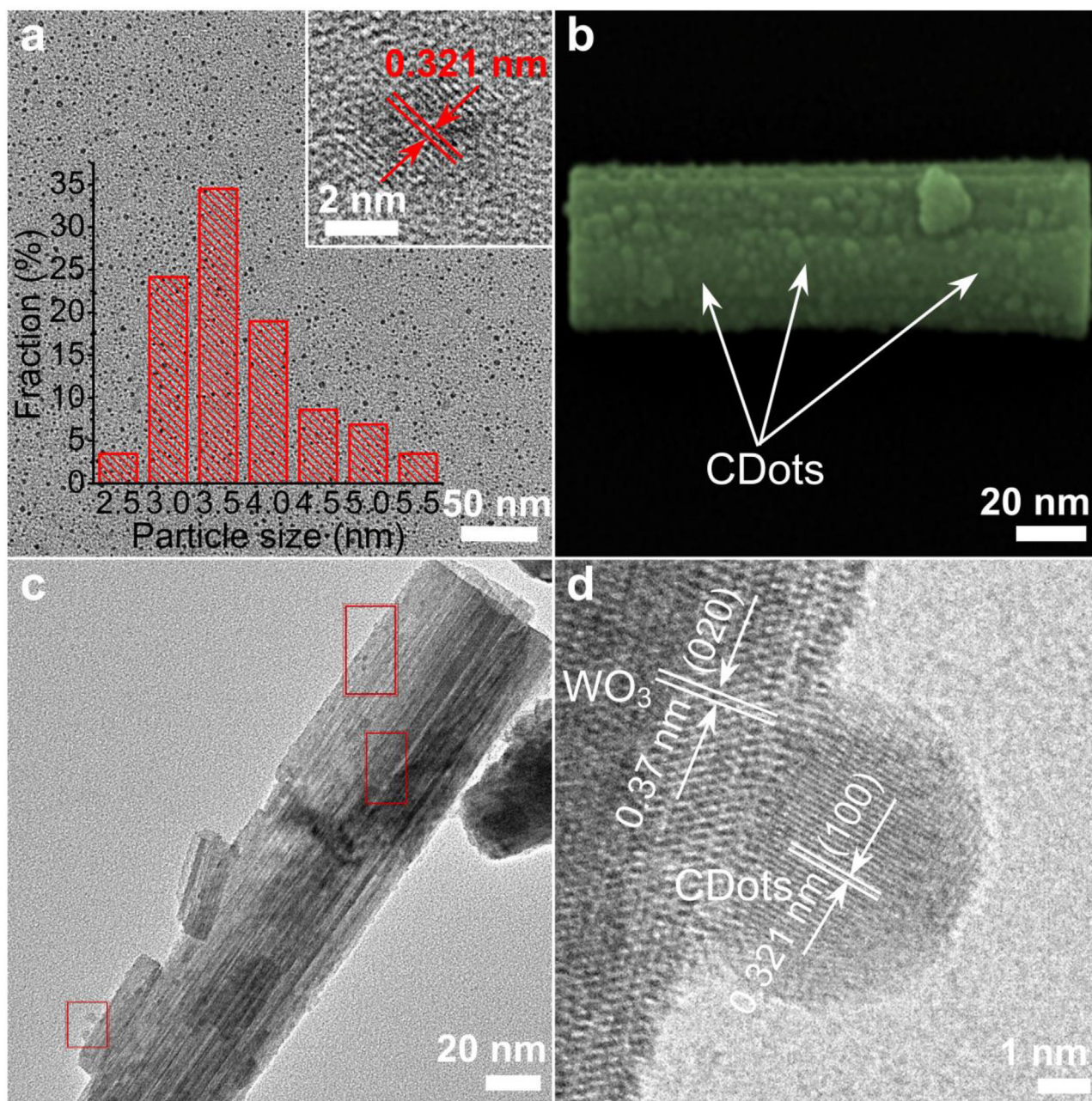


Fig. 1. (a) TEM and HRTEM images with size distribution of CDots. Inset is the size distribution analyzed from multiple images. (b) SEM image of as-prepared CDots/WO₃. TEM (c) and HRTEM (d) images of the CDots/WO₃. Some representative spots were marked in red box in TEM image. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of abundant functional groups on the surfaces of the CDots. A broad peak spanning 3250–3700 cm⁻¹ indicated that the surfaces of the CDots were rich in –OH groups [14]. The peaks found at 1404 cm⁻¹ may also have been caused by the existence of –OH [14]. In addition, several peaks were observed at around 1245 cm⁻¹ (C–O–C), 1634 cm⁻¹ (C=O), 1718 cm⁻¹ and 1441 cm⁻¹ (C=C), and 1400 cm⁻¹ (C–O) [28]. The presence of the corresponding hydrophilic oxygen-containing groups was presumably conducive to the facile and homogeneous dispersion of the CDots in the aqueous solution, thus helping the CDots to combine uniformly with the main semiconductor [30]. In summary, the above results indicated that oxygen-containing functional groups were formed by electrochemical oxidation. In this process, a certain amount of the (sp²-hybridized) C=C bonds in graphite was decomposed into oxygen-containing functional groups in the CDots [28].

As shown in Fig. 2b, peaks appeared at 2900–3600 cm⁻¹ for both WO₃ indicating the O–H stretching vibrations of –OH group, and for CDots/WO₃ suggesting the C–H and O–H stretching vibrations of the COH group, respectively [29]. The set of peaks below 1100 cm⁻¹ can be ascribed to the O–W–O stretching modes of WO₃ [5]. The peaks at 3425 cm⁻¹ that appeared in both WO₃ nanorods and CDots/WO₃ were attributed to the vibrations of surface-adsorbed water [31]. In the FT-IR spectra of CDots/WO₃, the absorption bands at 1635 cm⁻¹ were associated with the stretching vibrations of C=O, a consequence of the CDots [28,31]. It is worth noting that the peaks located at 1400 cm⁻¹ in the CDots, corresponding to the C–O stretching vibration, shifted to 1413 cm⁻¹ and were enhanced in intensity in the CDots/WO₃ nanocomposites [31]. We interpret this as further evidence of the strong interaction between CDots and WO₃ nanorods in the nanocomposites, as

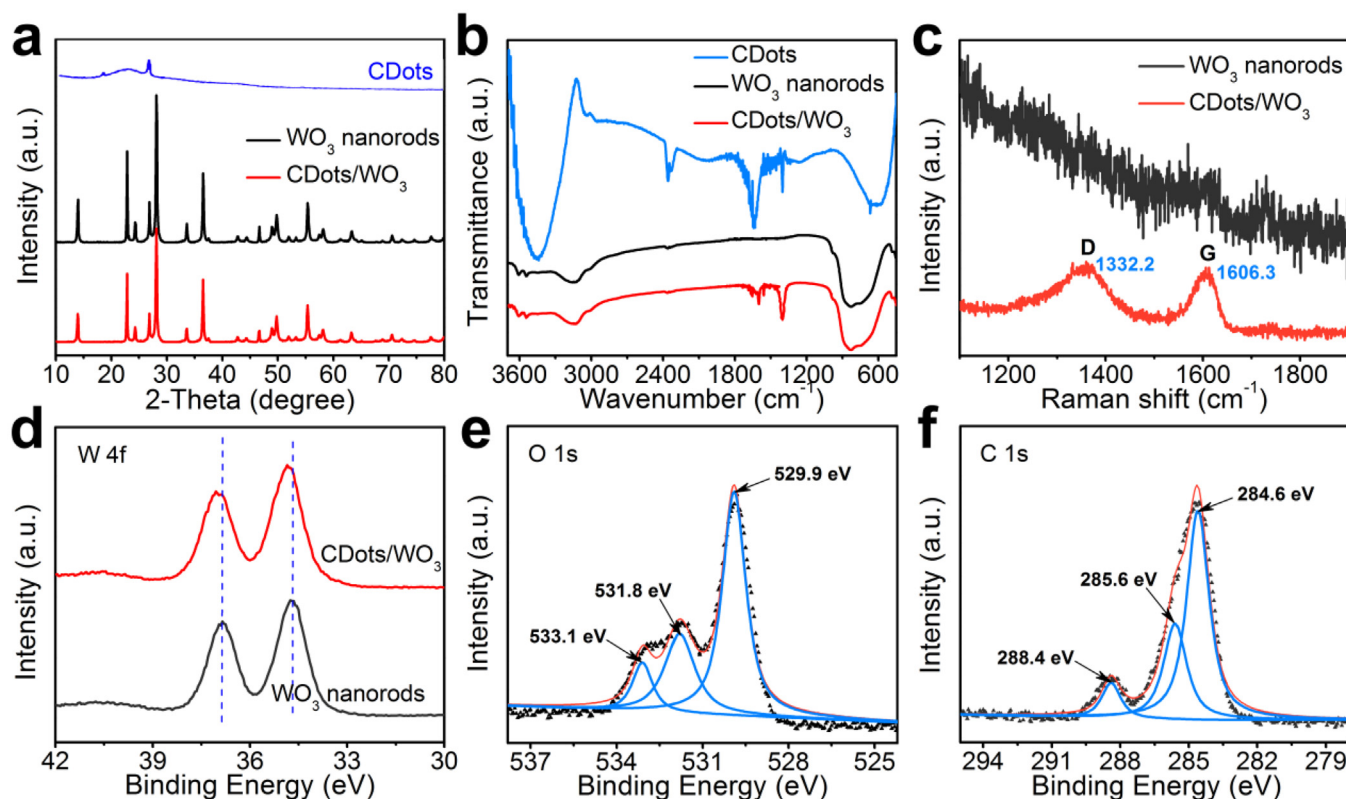


Fig. 2. The interaction between CDots and WO₃ nanorods. a, Room temperature XRD patterns and b, FT-IR spectra of CDots, WO₃ and CDots/WO₃ nanocomposites, c, Raman spectra of WO₃ and CDots/WO₃ nanocomposites. XPS spectra for WO₃ and CDots/WO₃ nanocomposites, high-resolution XPS spectra of d, O 1s, e, W 4f and f, C 1s.

follows: after the CDots were deposited on the surface of the WO₃ nanorods, new C–O bonds formed between them, with a different bond energy from the C–O bonds present in the isolated CDots [32]. This interaction thus caused a distinct peak shift.

The Raman spectra of the CDots/WO₃ nanocomposites (Fig. 2c) contained two characteristic peaks that were not present in the spectra of the WO₃ nanorods, located at about 1332.2 and 1606.3 cm^{−1}, corresponding to the D-band and the G-band, respectively [8,15]. The D-band arose from the vibrations of carbon atoms in disordered graphite, while the G-band was attributed to an ordered graphite structure [15]. The intensity ratio of the D band to the G band (I_D/I_G) is a measure of the ratio of sp³/sp² carbon in a sample, and shows the degree of graphitization of carbon. In the CDots/WO₃, this ratio was relatively high at 1.1. This indicated that the WO₃ crystal structure of the CDots/WO₃ nanocomposites contained a considerable amount of defects and lattice disorders corresponding to CDots, demonstrating the successful chemical combination of these two species [31].

The surface chemical composition of WO₃ and CDots/WO₃ samples, and the chemical interactions between CDots and WO₃ were further confirmed by XPS analysis. The full XPS spectrum of CDots/WO₃ (Fig. S5) confirmed the existence of O, W and C in the materials. For WO₃ sample, the binding energies at 35.5, 37.5 and 41.7 eV corresponded to the spin–orbit splitting of the W 4f_{7/2}, W 4f_{5/2} and W 5p_{3/2} components of tungsten oxides, respectively (Fig. 2d), suggesting that W⁶⁺ was the dominant valence state of W in the product [5]. The W 4f peak in the CDots/WO₃ nanocomposites exhibited a slight shift when compared to those in the WO₃ sample. This suggested that the surface chemical environment of W in the CDots/WO₃ changed, which could be attributed to the presence of interaction between the CDots and WO₃ [5,33]. The broad peak in the O 1s spectrum (Fig. 2e) could be resolved into three peaks centered at 529.9, 531.8 and 533.1 eV, which were identified

as the characteristic peaks of W–O, C=O and O–H bonds, respectively [5,29]. Fig. 2f displayed the XPS spectrum of the C 1s, which revealed the surface function groups on the CDots. Three peaks located at 284.6, 285.6 and 288.4 eV were attributed to C=O, C–C and sp²-hybridized carbon, respectively [5,20].

From XRD, Raman, FT-IR and XPS analyses, it is obvious that the bonding between CDots and WO₃ nanorods was efficiently formed, which was confirmed as the key to enhance the electronic separation and improve the photocatalytic activity by Wang et al. [1]. Taken together, these findings further confirmed the successful synthesis and the potential photocatalytic performance of the prepared CDots/WO₃ nanocomposites.

The light-response characteristics of the as-prepared materials were investigated by UV–vis–NIR DRS, PL spectroscopy, photocurrent measurements and EIS measurements. Fig. 3a presents the evidently strong, broad and continuous spectrum-wide absorption by the prepared CDots in the UV, visible and especially NIR regions. Thus, the composite photocatalyst containing CDots could effectively utilize solar energy to photo-generate electron–hole pairs. The weak peak at around 300 nm was the characteristic absorption peak of polycyclic aromatic hydrocarbons (π – π conjugated species), consistently with previous reports [29]. The DRS results thus provided further evidence that the CDots had formed from the aggregation of graphite fragments. The up-converted PL spectra (Fig. 3b) indicated that the CDots could be excited by long-wavelength light from 700 to 1000 nm, with the corresponding up-converted emissions located in the range from 345 to 575 nm, depending on the excitation wavelength. This excitation-dependent up-converted PL behavior of the CDots was probably attributable to the multiphoton active process, similar to that previously reported for carbon dots [13], which would enable the excited electrons to transfer to the acceptor (in contact with the sensitizer) either directly or indirectly.

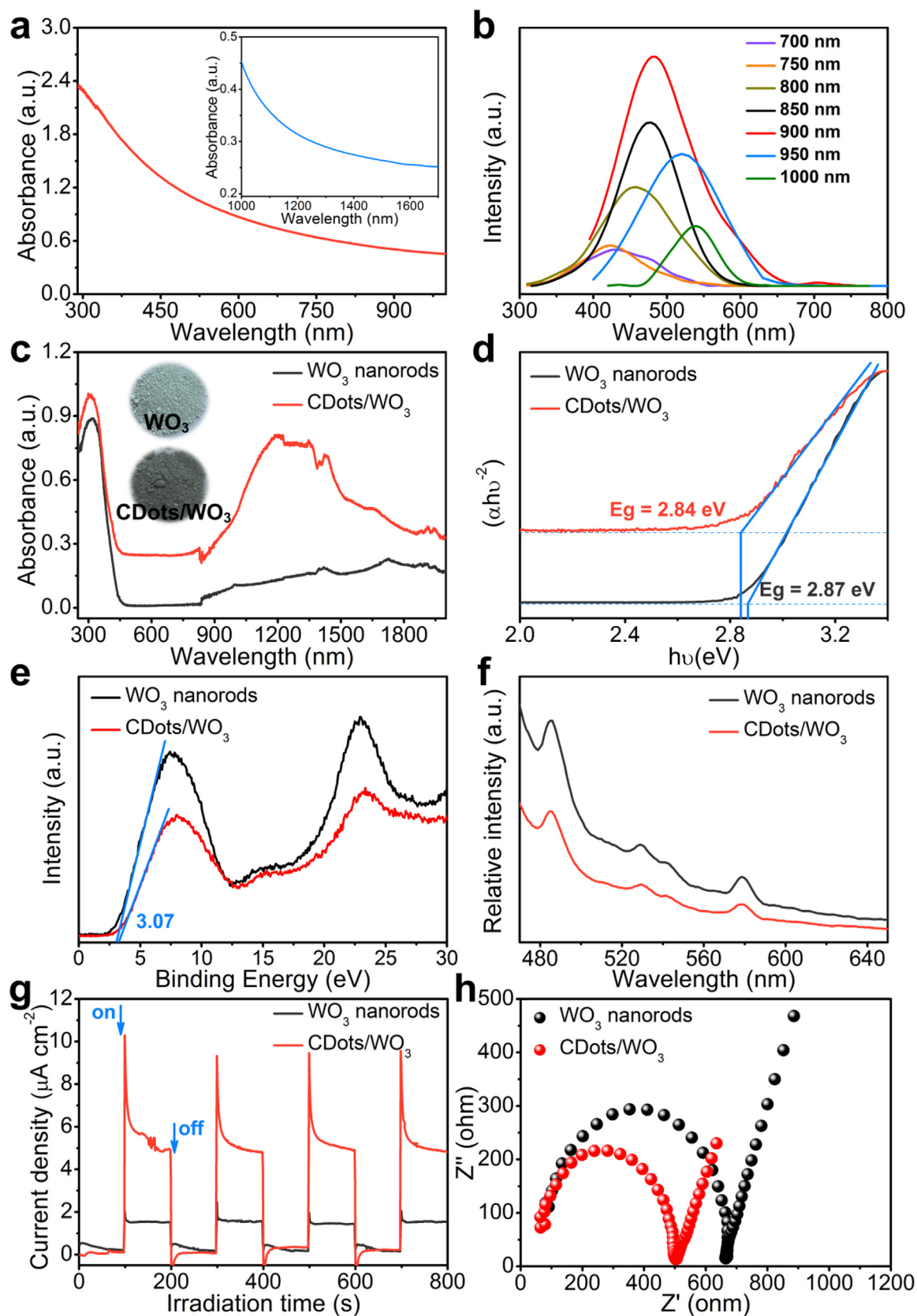


Fig. 3. Optical and charge migration properties of CDots, WO_3 nanorods and CDots/ WO_3 nanocomposites. a, UV-vis-NIR absorption spectrum of CDots. b, Up-converted PL spectra of CDots with different excitation wavelengths from 700 to 1000 nm with the interval of 50 nm. c, UV-vis-NIR DRS with insets for the colors of prepared samples; d, Band gap values, estimated from the plotted curve of $(\alpha h\nu)^{1/2}$ vs $h\nu$; e, XPS valence band spectrum; f, PL spectra; g, Transient photo-current response and h, Electrochemical impedance spectroscopy.

Fig. 3c compares the UV–vis–NIR DRS spectra of WO₃ and CDots/WO₃, in which the prepared CDots/WO₃ showed much greater light absorption across the entire examined spectral region. The WO₃ nanorods only appreciably absorbed visible light with wavelengths shorter than 475 nm, in agreement with a previous report [24]. In contrast, the CDots/WO₃ showed intense and wide absorption across the UV–vis region, implying the production of more photo-generated electron–hole pairs and a higher photocatalytic activity under this wavelength of irradiation. Unlike the WO₃ nanorods, the CDots/WO₃ showed continuous strong absorption in the NIR region (780–2000 nm), which is conducive to the full-spectrum utilization of solar light. The CDots evidently played an important role in enhancing the light-absorption capacity of the CDots/WO₃, as the absorption intensity increased with the increment in the amount of CDots (Fig. S6).

As shown in Fig. 3d, the optical band gaps (E_g) of the WO₃ nanorods and CDots/WO₃ were calculated as the slopes of the curves of converted $(\alpha h\nu)^r$ versus $h\nu$, where α , h and ν are the absorption coefficient, Planck constant and light frequency, respectively, and $r = 1/2$ for an indirect-band-gap material and $r = 2$ for a direct-band-gap material [34]. In our case, good linear fits were obtained when using $r = 2$, in agreement with previous reports describing WO₃ as a direct-band-gap material. The resulting calculated E_g values of the WO₃ nanorods and CDots/WO₃ were 2.87 and 2.84 eV (represented by the black and red curves in Fig. 3d), respectively. The similar E_g values indicated that the optical band gap of the WO₃ nanorods remained almost completely unchanged after the addition of CDots. In addition, the DRS spectrum of the CDots/WO₃ displayed an obvious tail between 2.3 and 2.8 eV, implying an enhanced photo-response and photocatalytic efficiency. Furthermore, we used the XPS valence band spectra of the WO₃ nanorods and CDots/WO₃ to determine their VB gaps (E_v), and both were calculated to be approximately 3.07 eV (Fig. 3e). This allowed the CB gaps (E_c) of the WO₃ nanorods and CDots/WO₃ to be estimated at 0.23 and 0.20 eV, respectively, from $E_c = E_v - E_g$. According to Wang et al. [1], a relatively high CB gap is favorable for heterostructure formation and charge-carrier transport. In addition to an appropriate band gap, the proper matching of the CB and VB levels of a photocatalyst with the redox potentials of the desired photocatalytic reactions is also important for photocatalytic degradation [1,7].

Fig. 3f presents the PL spectra of the WO₃ and CDots/WO₃. Both exhibited an emission peak centered at around 480 nm under excitation at 325 nm, in good agreement with the position of the absorption edge in the UV–vis–NIR DRS spectra (Fig. 3c). The intensity of the emission peak for the CDots/WO₃ decreased significantly compared with that for the WO₃ nanorods, indicating that the CDots on the surface of the WO₃ nanorods facilitated electron transfer and inhibited the recombination of the photo-generated charge carriers [5,25].

It was also confirmed by the photo-current and EIS measurements (Fig. 3g and h) that the introduction of CDots reduced the electron–hole recombination rate. The photo-current responses of both electrodes changed considerably once the light was switched on/off, with steady and reproducible results during several consecutive on–off irradiation cycles (Fig. 3g). The photo-current intensity of the CDots/WO₃ was ~ 2.9 times higher than that of the WO₃ nanorods, suggesting a higher separation rate of photo-excited electrons and holes in the CDots/WO₃ nanocomposites under visible-light irradiation [27]. A possible mechanism of this separation was that, after the photo-generated electrons were excited from the VB to the CB of WO₃, they were then transferred to the CDots, inhibiting the direct recombination of electrons and holes. The CDots were likely to have been good electron acceptors because of their conjugated π structure, making them efficient separation centers of the photo-excited charge carriers [30]. EIS measurements

of the WO₃ nanorods and CDots/WO₃ nanocomposites were carried out to investigate the process of electron transfer (Fig. 3h). The arc radius of the EIS Nyquist plot of the CDots/WO₃ was much smaller than that of the WO₃ nanorods, implying a faster rate of interfacial charge transfer to the electron acceptors in the former, resulting in the effective separation of electron–hole pairs [5,8].

3.2. Photocatalytic performance

As shown in Fig. 4a–c, the concentration of RhB showed no appreciable change under UV, visible or NIR irradiation, indicating that the RhB was photo-chemically stable. The prepared WO₃ nanorods and CDots/WO₃ achieved $\sim 20\%$ and 25% removal efficiency of RhB by adsorption, respectively, with no apparent adsorption over pure CDots or commercial WO₃ nanoparticles (Fig. 4a–c).

Whether under UV, visible-light or NIR irradiation, the removal efficiencies of RhB always decreased in the order CDots/WO₃ > prepared WO₃ nanorods > commercial WO₃ nanoparticles. For instance, under visible light, the CDots/WO₃ nanocomposites exhibited an RhB removal efficiency of 99.1% in 140 min, while the corresponding efficiencies of the WO₃ nanorods and commercial WO₃ were 69.1% and 11.6%, respectively, under the same condition. The CDots/WO₃ showed higher photocatalytic activity than the WO₃ nanorods under both UV and visible-light irradiation, mainly because of the stronger light absorption and the more efficient electron-transfer capability of the CDots/WO₃ (Fig. 3). Moreover, the CDots/WO₃ presented significant capability for photocatalytic RhB degradation (61.2% in 480 min) under light wavelengths longer than 780 nm (NIR light), while neither the WO₃ nanorods nor commercial WO₃ achieved any noticeable degradation. These results demonstrated that the introduction of CDots significantly improved the photocatalytic activity of the WO₃ nanorods under a broad spectrum of light including UV, Vis and NIR frequencies. By contrast, in WO₃ nanorods, only light with wavelengths shorter than 475 nm could be used to photo-generate electron–hole pairs; therefore, the up-converted PL behavior of the CDots effectively extended the photo-active wavelengths of the CDots/WO₃ to the NIR region. To quantitatively understand the degradation of RhB, the degradation kinetics was investigated by fitting the experimental data to the Langmuir–Hinshelwood model under UV, visible and NIR irradiation (Fig. S8 and Table S2) [35]. The CDots/WO₃ possessed a higher apparent reaction rate constant (k value) than those of the prepared WO₃ nanorods and commercial WO₃ nanoparticles, indicating higher activity under UV, visible and NIR irradiation. In addition, the mineralization efficiency of RhB were $\sim 88.1\%$, 89.8% and 45.3% for CDots/WO₃ under UV, visible and NIR light irradiation, which were much higher than other materials under the identical conditions (Fig. S9).

To eliminate the effect of dye photo-sensitization and further evaluate the application potential of CDots/WO₃, tests were performed using TCH and phenol as the target pollutants. The prepared WO₃ nanorods exhibited a TCH removal efficiency of only 40.8% in 3.5 h under visible-light irradiation, while the CDots/WO₃ achieved a roughly 2-fold higher efficiency (78.6%) under the same conditions (Fig. 4d). The fitting of the TCH degradation to the Langmuir–Hinshelwood model is shown in Table S2 and Fig. S10. The calculated k value for the CDots/WO₃ nanocomposites was 0.403 h^{-1} , which was 2.9 times higher than that of the WO₃ nanorods (0.139 h^{-1}). The phenol removal efficiencies were $\sim 70.2\%$ and 34.7% for the CDots/WO₃ and WO₃ nanorods, respectively, under visible-light irradiation in 4 h (Fig. 4e). The calculated k values showed similar trends (Fig. S10 and Table S2). Also, Fig. 4f shows that the mineralization efficiency of phenol by the CDots/WO₃ was 55.9%, much higher than that by the WO₃ nanorods (20.0%). These results clearly demonstrated that the photocatalytic activity of the

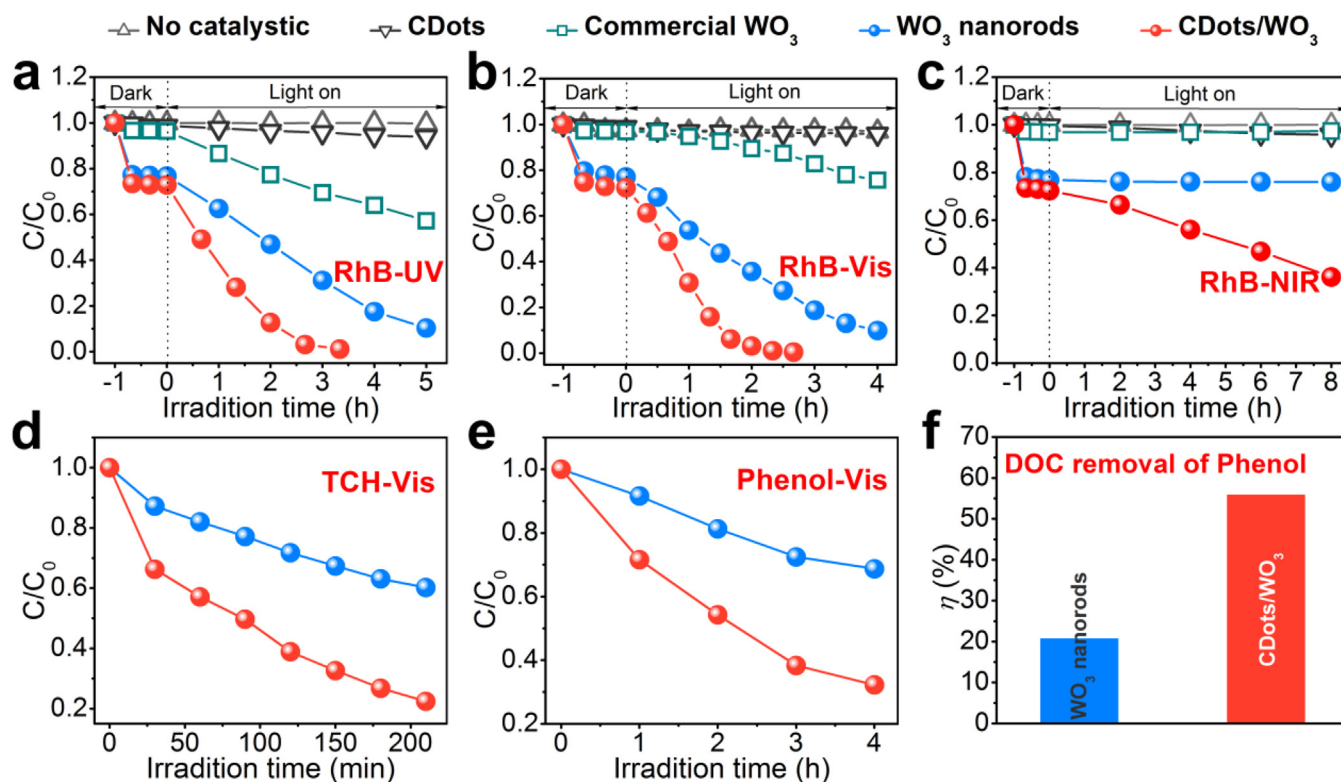


Fig. 4. Photocatalytic degradation of RhB by prepared WO₃ and CDots/WO₃ under a, UV, b, visible, and c, NIR light irradiation; and d, e and f Photocatalytic degradation of TCH, phenol and DOC removal efficiency of phenol under visible light irradiation. Photocatalytic degradation conditions: 100 mL solution (10 mg L⁻¹ RhB, 20 mg L⁻¹ TCH and 20 mg L⁻¹ phenol), light source (150 W xenon lamp with different emission region by various filters as presented in Fig. S1), pH (neutral), temperature (ca. 20 °C), magnetic stirring rate (500 rpm).

WO₃ nanorods was markedly improved after the deposition of CDots, and that the CDots played an important role in the activity of the CDots/WO₃ nanocomposites.

3.3. Photocatalytic mechanism

To investigate the photocatalytic mechanism of the CDots/WO₃ nanocomposites, scavenger-quenching experiments were performed to compare the photocatalytic capabilities of each of the reactive oxidation species (ROSs) potentially involved in the reaction. The proposed ROSs, namely, e^- , $\cdot O_2^-$, $\cdot OH$ and h^+ , were quenched using four different scavengers: Cr⁶⁺, TEMPO, isopropanol and sodium oxalate, respectively. First of all, it was worth noting that the reaction time for WO₃ and CDots/WO₃ were 260 and 160 min, respectively. As shown in Fig. 5, e^- and h^+ were the main ROSs present in the WO₃ nanorods system, while $\cdot O_2^-$ and $\cdot OH$ were scarce. In contrast, all four types of ROS were present in the CDots/WO₃ nanocomposite system, which was consistent with the faster photocatalytic rate of this system compared with the WO₃ nanorods (Fig. 5). In the CDots/WO₃ system, the effect of the scavengers on the reaction rate decreased in the order sodium oxalate (for h^+) > TEMPO (for $\cdot O_2^-$) > isopropanol (for $\cdot OH$) > Cr⁶⁺ (for e^-). Comparing the WO₃ nanorods with the CDots/WO₃, h^+ was an important ROS in both systems, while the e^- concentration was sharply reduced in CDots/WO₃. However, the emergence of $\cdot O_2^-$ and $\cdot OH$ in the latter indicated that they played a critical role and made a large contribution to the photo-degradation of RhB. The emergence of both these ROSs in CDots/WO₃ may have been a consequence of the fast electron transfer rate. The additional photo-generated electrons may have combined with the adsorbed O₂ to form $\cdot O_2^-$, thus greatly enhancing the photocatalytic performance. Moreover, the fast electron transfer rate may have promoted the

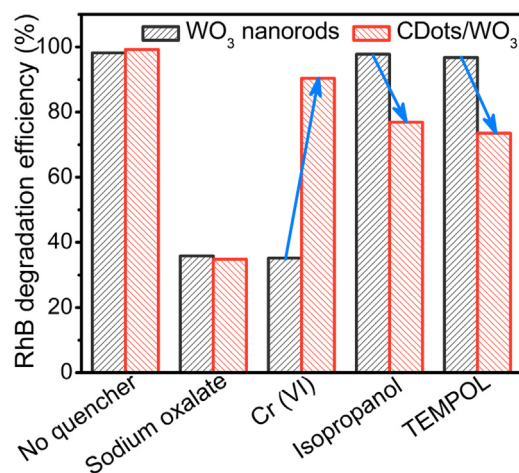


Fig. 5. Quenching experiment of active-species during the photocatalytic degradation of RhB over WO₃ nanorods and CDots/WO₃ under visible light irradiation. Photocatalytic degradation conditions: (100 mL solution of 10 mg L⁻¹ RhB), light source (filtered 150 W xenon lamp with visible light emission only), pH (neutral), temperature (ca. 20 °C), magnetic stirring rate (500 rpm) and reaction time (160 min for CDots/WO₃ and 260 min for WO₃ nanorods).

generation of $\cdot OH$ from both h^+ and $\cdot O_2^-$, thus further enhancing the photo-degradation rate. It was worth mentioning that almost no $\cdot O_2^-$ and $\cdot OH$ were present in the WO₃ nanorods system, indicating that the WO₃ nanorods were unable to generate those ROSs under visible-light irradiation. However, after the introduction of CDots, both $\cdot O_2^-$ and $\cdot OH$ appeared in the CDots/WO₃ system, having most likely been produced on the surface of the CDots.

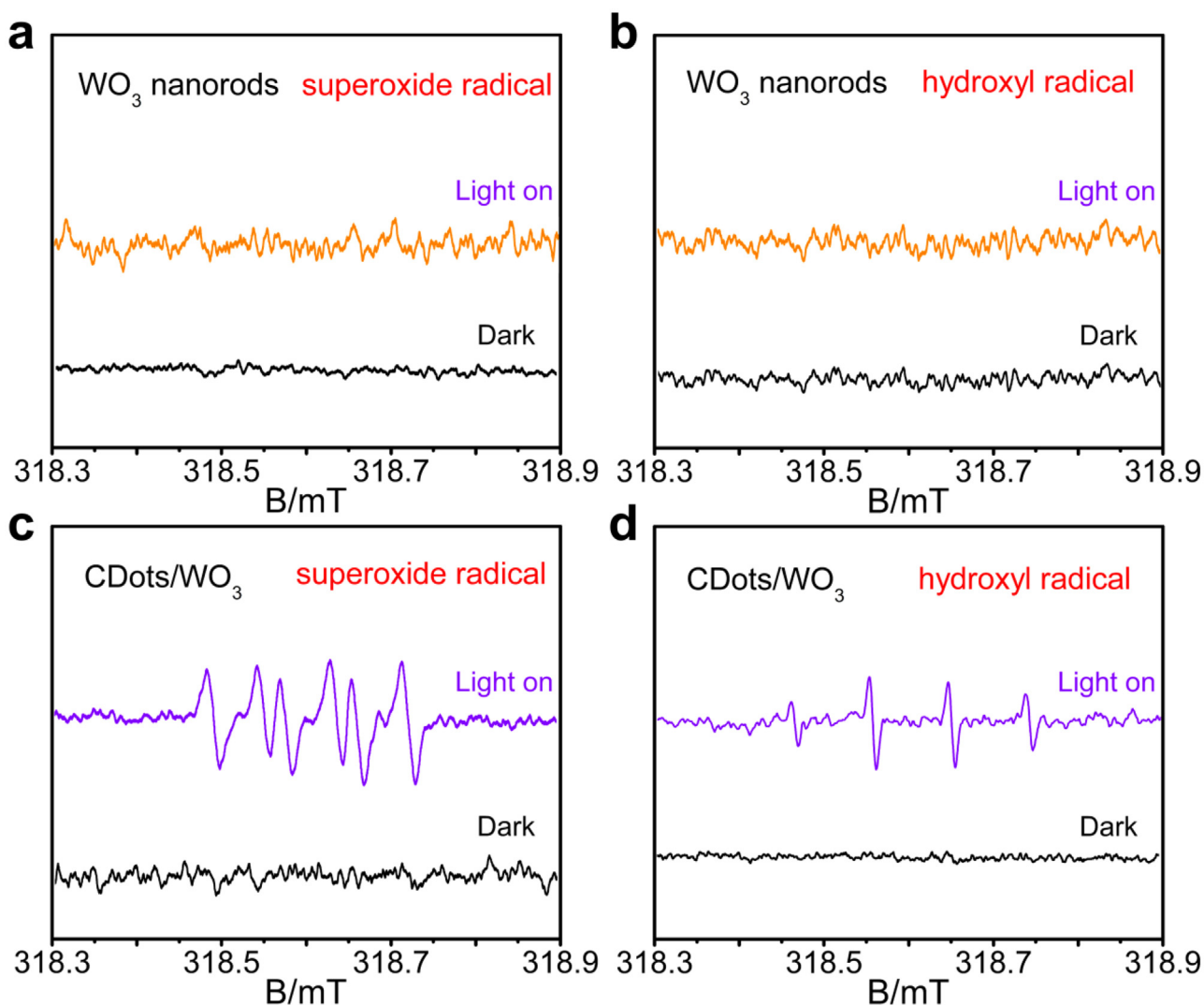


Fig. 6. DMPO spin-trapping ESR spectra recorded with (a and b) WO_3 nanorods and (c and d) CDots/WO_3 nanocomposites under visible light irradiation. The dispersion solutions were methanol and water for the detection of $\text{DMPO}\cdot\text{O}_2^-$ and $\text{DMPO}\cdot\text{OH}$, respectively).

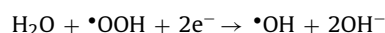
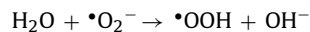
To further confirm the active species and reveal the photodegradation mechanism on the photoreaction process, the ESR spin-trap technique was then performed for WO_3 nanorods and CDots/WO_3 nanocomposites with DMPO in methanol and H_2O . DMPO is a nitron spin trap generally used for trapping radicals due to the generation of stable free radicals, $\text{DMPO}\cdot\text{O}_2^-$ or $\text{DMPO}\cdot\text{OH}$ [33]. As shown in Fig. 6a and b, negligible signals of $\text{DMPO}\cdot\text{O}_2^-$ and $\text{DMPO}\cdot\text{OH}$ were found for WO_3 , revealing that $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ may be not the main active species under visible light irradiation. It was consistent with the results of scavenger-quenching experiments (see Fig. 5). In contrast, after the modification of CDots on the WO_3 , both the signal of $\text{DMPO}\cdot\text{O}_2^-$ and $\text{DMPO}\cdot\text{OH}$ can be found clearly (Fig. 6c and d). It indicated that the $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ were produced in the CDots/WO_3 system, which contributed to the higher photocatalytic activity of CDots/WO_3 materials [33].

The standard redox potential of $\text{O}_2/\cdot\text{O}_2^-$ has been established as -0.33 V (vs. NHE). Thus, in order to generate $\cdot\text{O}_2^-$ on the surface of a semiconductor photocatalyst, the CB position should be more negative than this value. However, the CB of the prepared WO_3 nanorods was positioned at about 0.23 eV , far more positive than the reduction potential of $\text{O}_2/\cdot\text{O}_2^-$. Thus, the photo-generated electrons (e^-) on the surface of the WO_3 nanorods were thermodynamically unable to react with O_2 to produce $\cdot\text{O}_2^-$. The $\cdot\text{O}_2^-$

would appear only if the CB potential was satisfied with the thermodynamic potentials of $\text{O}_2/\cdot\text{O}_2^-$. In contrast, a significant amount of $\cdot\text{O}_2^-$ appeared in the CDots/WO_3 nanocomposite system, suggesting that the CDots acted as a co-catalyst, with an appropriate CB position to produce $\cdot\text{O}_2^-$. Indeed, previous studies have confirmed that the CB in CDots is positioned at around -1.16 eV [25]. Therefore, the e^- generated in the CB of the CDots could react with O_2 to produce $\cdot\text{O}_2^-$. This was consistent with the results of the scavenger-quenching experiments and ESR analysis (Figs. 5 and 6). Similarly, the VB position of the WO_3 nanorods was $+3.07\text{ eV}$, which was more positive than the standard redox potential of $\cdot\text{OH}/\text{OH}^-$ (2.3 eV vs. NHE). In theory, $\cdot\text{OH}$ could have formed on the surface of the WO_3 nanorods through the following reaction:



However, almost no $\cdot\text{OH}$ was present in the WO_3 nanorods system. In contrast, $\cdot\text{OH}$ was detected when the CDots/WO_3 was used as the catalyst. The $\cdot\text{OH}$ that appeared in the CDots/WO_3 system was therefore produced by the following reactions:



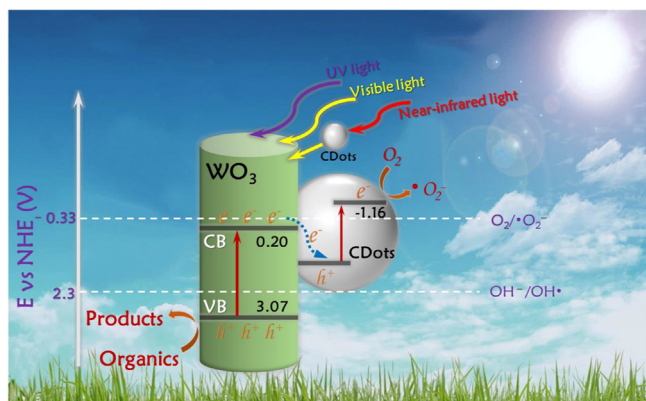
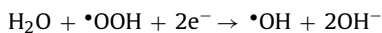
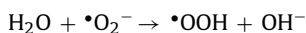
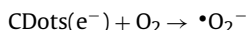
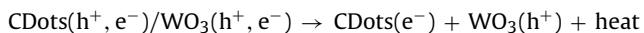
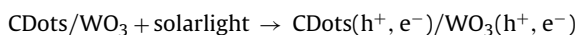


Fig. 7. Schematic photocatalytic mechanism for the CDots/WO₃ nanocomposites under UV, visible and NIR light irradiation.

On the basis of the above results, a charge-transfer mechanism for the CDots/WO₃ nanocomposite was proposed, as shown in Fig. 7. In the CDots/WO₃ heterostructure, part of the surface of the WO₃ nanorods was covered by CDots, constituting a CDots/WO₃ Z-scheme photocatalytic system. Under solar irradiation, both WO₃ and CDots were photo-excited, generating e[−]/h⁺ pairs. The h⁺ generated in WO₃ remained in the VB of WO₃. However, the e[−] in the CB of WO₃ transferred to the VB of the CDots, and combined with the h⁺ in the VB of the CDots through the contact interface between CDots and WO₃ nanorods. Accordingly, the efficient spatial separation of the photo-generated e[−]/h⁺ pairs was realized. Subsequently, the h⁺ stored in the VB of WO₃ migrated to the surface of WO₃ and directly decomposed the surface-adsorbed organics, while the enriched e[−] content in the CB of the CDots likely favored the generation of •O₂[−] (which also promoted degradation of the organics) because of the reduced electron–hole recombination. Thus, the oxidation and reduction of the organic pollutants occurred separately on the surfaces of the two different materials. Based on the discussion above, the major reactions in this system would have been as follows:



No electron mediator was present between the WO₃ nanorods and CDots; rather, the photo-generated e[−] transferred directly through the interfacial contact. This Z-scheme heterostructure not only promoted the separation of photo-generated e[−]/h⁺ pairs but also improved the redox ability of the photocatalyst because of the enhanced redox potential. The formation of a Z-scheme heterostructure effectively extended the lifetime of the photo-generated charge carriers, thus promoting the redox ability of the system [27,36].

In contrast, if WO₃ and CDots had formed a conventional CDots/WO₃ heterostructure (Type-II), the photo-generated e[−] would have transferred from the CB of the CDots to the CB of the WO₃ nanorods spontaneously. The h⁺ in the VB of the WO₃ nanorods would have transferred to the VB of CDots to form a Type-II heterostructure. Although the spatial separation of the photo-generated e[−]/h⁺ pairs would still have been achieved, it would have weakened the redox potential of photocatalysis [36]. In

this case, the e[−] gathered on the surface of the WO₃ nanorods would have been unable to combine with O₂ to generate •O₂[−] because of the lower CB potential of the system. As a result, no •O₂[−] would have been detected in a Type-II CDots/WO₃ system, in contradiction to the experimental finding (see in Figs. 5 and 6). Therefore, it can be concluded that the WO₃ nanorods and CDots did not form a Type-II heterostructure. Instead, the mechanistic evidence indicates that a direct Z-scheme photocatalytic system was formed in the CDots/WO₃.

In the above discussion, we have proposed a complete photocatalytic mechanism for the CDots/WO₃ nanocomposites under UV, visible and NIR irradiation (Fig. 7). Three main processes occurred in the CDots/WO₃ nanocomposites under solar irradiation. (1) Both WO₃ nanorods and CDots could be excited by UV and short-wavelength visible light, thus photo-generating e[−]/h⁺ pairs. Moreover, the CDots could also efficiently absorb longer-wavelength visible and NIR light, which was then transformed by up-conversion into shorter-wavelength light, which in turn was absorbed by the WO₃ nanorods to produce additional photo-generated e[−]/h⁺ pairs. Hence, the entire spectrum of solar light energy could be utilized efficiently. (2) A direct Z-scheme heterostructure was formed after the CDots were introduced to the surface of the WO₃ nanorods. This contact interface resulted in the recombination of the photo-generated e[−] in WO₃ with the h⁺ in the CDots, preventing the recombination of e[−]/h⁺ pairs from WO₃. Therefore, a greater amount of e[−] with a relatively low CB potential, as well as h⁺ with a relatively high VB potential, could be retained, which contributed to the enhanced photocatalytic ability. Furthermore, the spatial separation of e[−]/h⁺ pairs ensured that the oxidation and reduction reactions occurred in two different regions. (3) The organic pollutants in the solution were efficiently adsorbed by the large number of active sites in CDots/WO₃. In turn, the organics were effectively oxidized and hence removed by the generated ROSs, including e[−], h⁺, •OH and •O₂[−]. The pollutants were degraded to intermediate products or even to H₂O and CO₂ after the processes of aromatic-ring opening.

3.4. Recycling reactions

Two of the most important parameters for the practical application of a photocatalyst are its stability and reusability. Cycling tests of RhB photo-degradation were thus performed under UV, visible and NIR irradiation. As depicted in Fig. 8a, the activity of the CDots/WO₃ nanocomposites remained almost unchanged after 5 cycles under identical experimental conditions, i.e., the RhB removal efficiencies varied from 99.7% to 97.1% under UV light in 200 min, 99.6% to 97.7% under visible light in 160 min and 62.7% to 60.1% under NIR light in 480 min. This demonstrated that the prepared photocatalyst was stable, even with long reaction durations. Moreover, both the CDots/WO₃ and WO₃ nanorods exhibited high stability and reusability (Figs. 8 a and S11), with only slight decreases of the degradation efficiency after 5 cycles. The physical structure and optical-absorption ability of the fresh and recycled CDots/WO₃ samples were also carefully compared by XRD, XPS and DRS analysis (Fig. 8b–d). There were no significant differences between the fresh and recycled samples, indicating the excellent robustness of the CDots/WO₃ nanojunction. The above results confirmed that the CDots/WO₃ nanocomposites were stable after repeated recycling.

4. Conclusion

In this paper, we successfully synthesized a direct Z-scheme CDots/WO₃ nanocomposite via a facile process for the first time. The as-prepared CDots/WO₃ exhibited strongly enhanced photo-

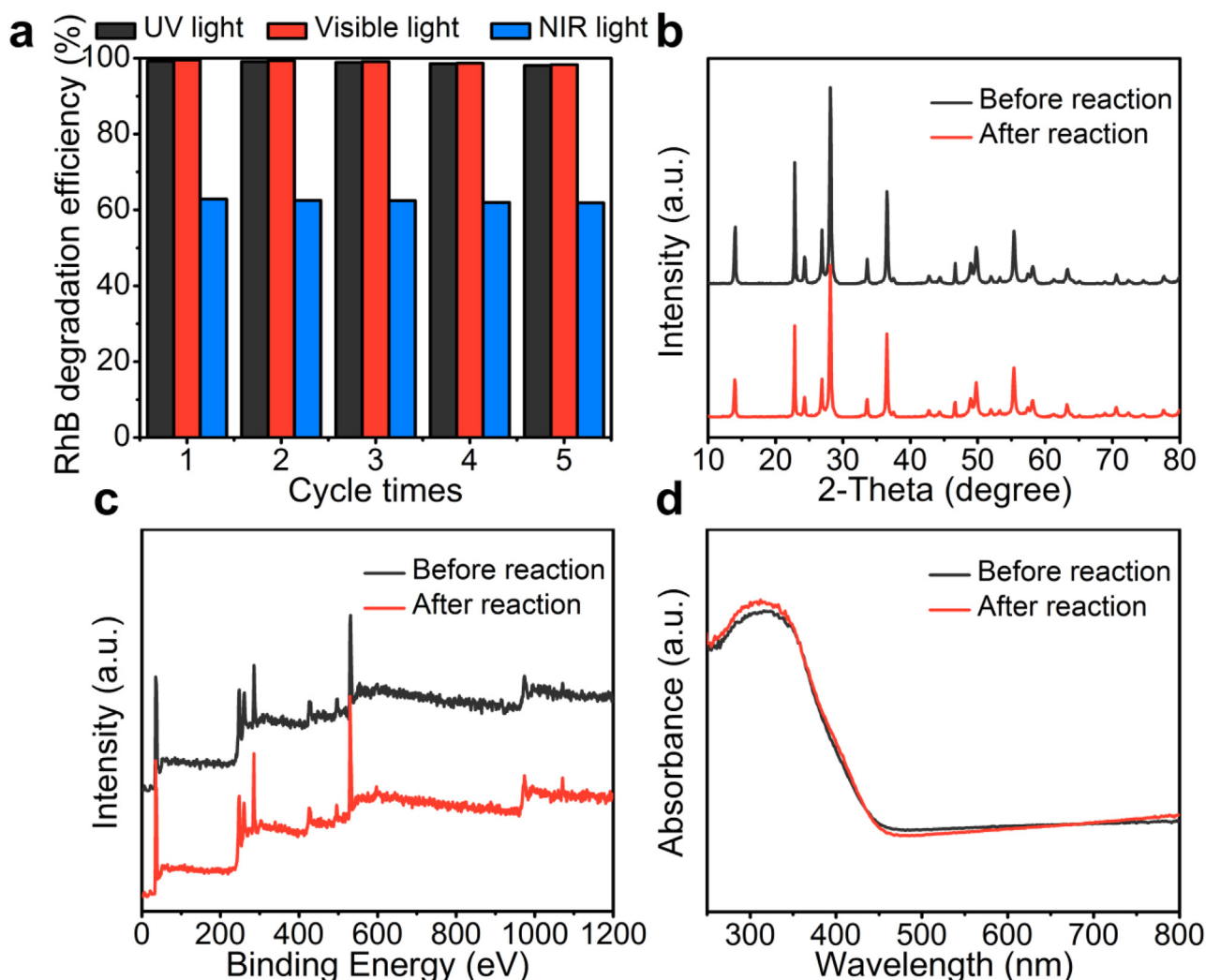


Fig. 8. Stability and reusability of CDots/WO₃ nanocomposites. a, Recycling runs of photocatalytic activity of the CDots/WO₃ nanocomposites toward RhB photo-degradation under UV, visible and NIR light irradiation. Physical characterizations of the CDots/WO₃ nanocomposites before and after the repeated photocatalytic degradation experiments in visible irradiation. b, XRD pattern; c, Full XPS spectra; d, UV-vis DRS spectra. Photocatalytic degradation conditions: 100 mL solution of 10 mg L⁻¹ RhB, light source (150 W xenon lamp with different emission region by various filters as presented in Fig. S1), pH (neutral), temperature (ca. 20 °C), magnetic stirring rate (500 rpm).

catalytic performance for the photo-degradation of RhB, TCH and phenol, and also showed increased mineralization efficiency, compared with the prepared WO₃ nanorods and commercial WO₃ nanoparticles under UV, Vis or NIR irradiation. On the basis of TEM, SEM, XPS, UV-vis-NIR DRS and PL analyses, scavenger-quenching experiments and ESR analysis, a possible mechanism was proposed for the photocatalytic reaction process. Two potential factors causing the improved performance of the system were identified, namely, its enhanced photo-response and effective spatial separation of photo-generated e⁻/h⁺ pairs. In summary, this work demonstrated that an all-solid-state direct Z-scheme CDots/WO₃ nanocomposite could be accurately prepared, and displayed an excellent photocatalytic performance, representing a crucial advance in the synthesis of Z-scheme photocatalytic systems.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.03.017>.

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